

## **MIS Small and Large Sample Surveillance 2001 Year End Report**

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### **Statement of work Scope:**

The object of this project is to assist in the establishment of parameters for safe storage of plutonium bearing materials in sealed containers under the DOE packaging and storage standard, for Materials Disposition and DOE sites (SRS, RFETS, Hanford, LANL, and LLNL). The complete surveillance of sealed containers will provide the DOE complex with mechanisms for gathering, interpreting, and reporting experimental storage data on plutonium-bearing materials. The materials studied include pure and impure oxides that are representative of materials that will be packaged for long-term storage. The information will support the DOE storage standard, the DOE Integrated Surveillance Plan and site-specific surveillance efforts. Appropriate R&D projects for Materials Identification and Surveillance (MIS) will also be supported by the information.

### **I. Introduction.**

The DOE standard for stabilization and packaging of Pu bearing materials, DOE-STD-3013-2000, [DOE 2000a] requires that each site assures that materials packaged according to the standard are represented in the 94-1 Material Identification and Surveillance (MIS) program. Sec. 6.6 of the 3013 Standard states that “...*the sites are responsible for assuring that oxides being packaged to this Standard are represented by the items accumulated in the MIS program.*” Additionally a requirement was set by the Defense Nuclear Safety Board stating that “*The Board believes that this requirement [representation in the MIS program] will play an important role in ensuring that the standard does not allow packaging of materials that could result in unsafe conditions during storage. The Board requests to be informed how this requirement will be implemented by DOE's field activities*”, John Conway.

The Los Alamos National Laboratory Shelf Life project was established under the MIS Program to define the behavior of Pu bearing material in sealed containers. Experience with Pu bearing materials has shown that gases generated by catalytic and/or radiolytic processes may accumulate [e.g. DOE 2000b, Eller 1999, Haschke 1995 and 1998]. Of concern are the generation of H<sub>2</sub> gas from adsorbed water, the generation of water in the vapor phase at elevated temperatures, and the generation of HCl or Cl<sub>2</sub> gases from the radiolysis of chloride-containing salts, which exist as impurities in the oxides. The combination of chloride bearing gases and condensed water may generate localized corrosion concerns within the 3013 package.

The Shelf Life project will monitor gases over oxide materials in a limited number of large-scale 3013 inner containers and in many small-scale containers with samples taken from site-wide representative materials actually being stored. The small-scale containers allow more sample types and conditions to be studied. For the large-scale study, baseline

plutonium oxides, oxides exposed to high-humidity atmospheres, and oxides containing chloride salt impurities are planned. [Worl 2000] This information provides invaluable, defensible results for assuring safe long-term storage of these materials in sealed containers. The results also provide a foundation and database input for the Integrated Surveillance Program [ISP 2001] for the 3013 container.

## **II. Results / Accomplishments.**

The LANL based shelf-life surveillance project has two parallel studies. Many small (10-g) samples are monitored for relatively short time periods, and a limited number of large samples equivalent in size to the 3013 storage can capacity will be monitored for long periods of time. The small samples will allow a database of many material types prepared according to various site-specific packaging methods to be compiled. Large-scale studies will give the behavior of a limited number of samples in the precise geometry and environment in which the material will be stored. Comparison between the two sample types will determine the degree of confidence in small sample experiments and fundamental measurements in predicting the long-term behavior of real materials.

The work conducted in this project is in accordance with LANL quality management criteria and defined in project specific documentation. [Worl 2001, Kreyer 2001]

### **Engineering Design**

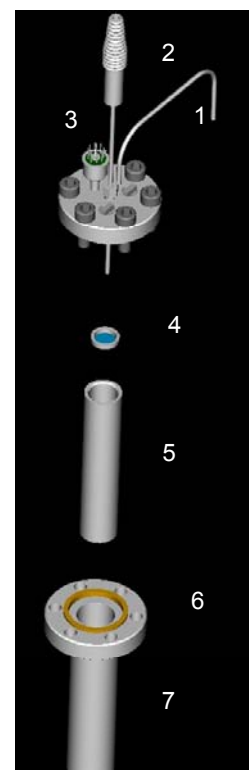
We have designed instrumented storage containers that mimic the inner storage can specified in the 3013 standard at both large- and small-scale capacities (2.3 liter and 0.0045 liter, respectively). The containers are designed to maintain the volume to material mass ratio while allowing the gas composition and pressure to be monitored over time. The large-scale cans are instrumented with a Raman fiber-optic probe, a gas chromatography (GC) / mass spectrometer (MS) sampling port, an acoustic resonance chamber, two corrosion monitors, and pressure and temperature sensors. Data collection for the large-scale containers is automated in order to reduce worker exposure. The small-scale containers are designed with a microliter gas-sampling capability and pressure and temperature sensors. These containers will be stored in a heated array in order to reproduce the increased temperatures arising from radioactive self-heating. Figure 1 shows the large- and small-scale containers.



**Figure 1.** Instrumented shelf life surveillance containers. Digital photograph of the small- (4.5 cc) and large- (~2300 cc) scale containers.

### ***Small-Scale Study Container Design.***

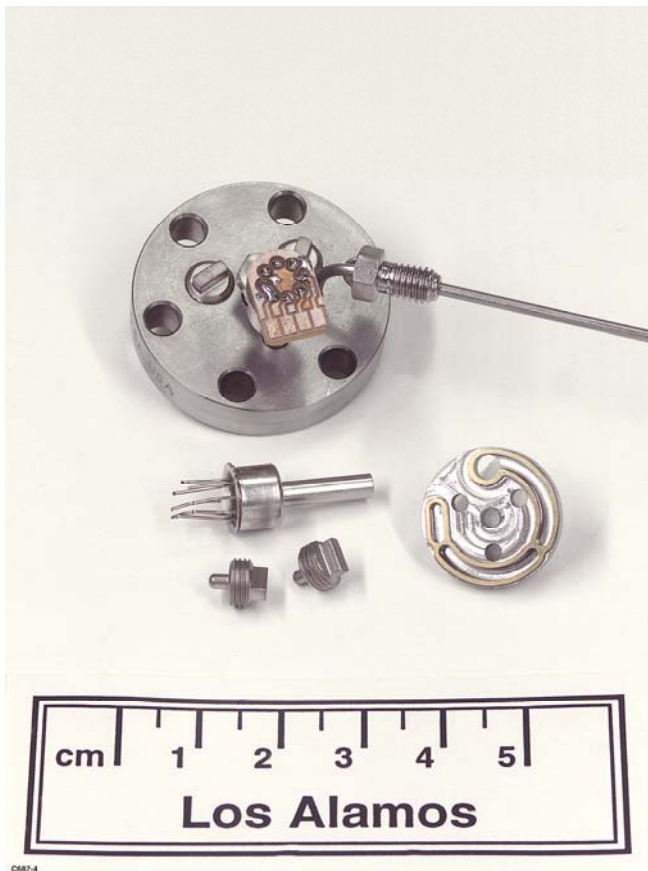
The small-scale container project has been ongoing by Allen et al to examine gas generation from plutonium oxide materials. [Mason 1999, Allen 1999] We have integrated this ongoing small-scale work with the large-scale study in order to provide continuity and increased effectiveness in both resources and data results. In the process of project integration, we have developed a redesign of the small-scale container so that the volume of the small-scale containers is 1:500 scaling of the BNFL inner container, a container configuration that satisfies the DOE 3013 Standard. The previous study utilizes a container that is approximately 60 ml in size containing 10 grams of oxide material. In order to maintain the correct ratio of total container volume to the maximum oxide fill volume, the small-scale container total volume should be 4.5 ml. Figure 2 depicts the redesign of the small-scale 3013 container. The containers are equipped with a 45-microliter gas-sampling chamber for gas analysis, pressure transducer and thermocouples. The pressure and temperature data are monitored continuously. A gas analysis will be conducted at periodic intervals with higher frequency occurring shortly after sample loading.



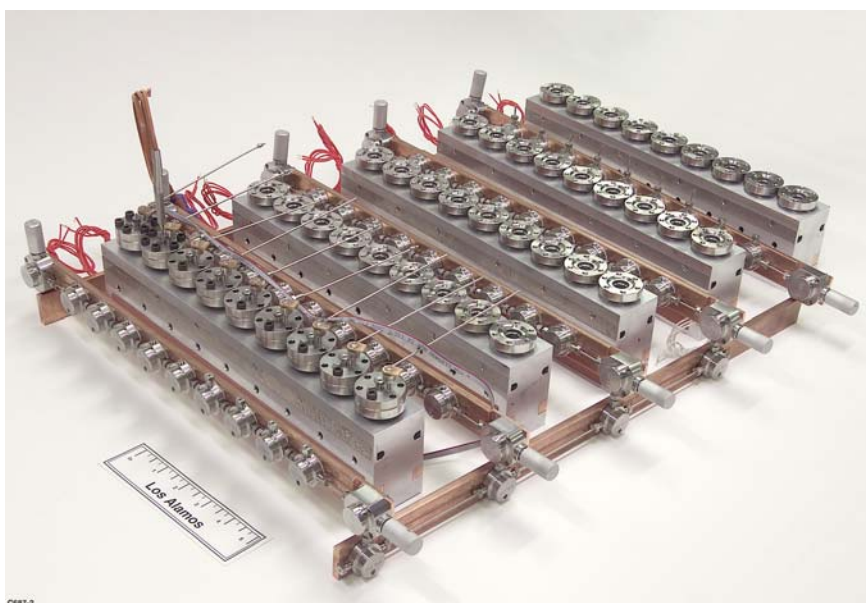
**Figure 2.** Design of the small-scale containers showing the 1) gas transfer line, 2) thermocouples, 3) pressure transducer, 4) thin foil cap, 5) inner container, 6) H<sub>2</sub> resistant gasket, and 7) outer container.

Details of the miniaturized lid assembly are shown in Figure 3. Customized valves and gas sampling chamber are required to meet the demands of a limited gas-volume for periodic sampling.

The small-scale reactors will be heated to accommodate the self-heating temperature that an analogous large-scale 3013 oxide filled container would generate. The heated five by nine array allows for five variable temperature controllers with nine containers each. The heating range is from room temperature to 85 °C. A figure of the array without insulation is shown in Figure 4. The tubing between the small containers and the gas analysis equipment is heated in order to avoid condensation of gases. The heaters were tested and subsequent heat transfer calculations assisted in the configuration of the insulation. [Cummings 2001]



**Figure 3.** Small-scale container lid assembly showing the 1) gas transfer line, 2) 45 µL gas sampling chamber, 3) miniaturized pressure transducer, and 4) customized valves.



**Figure 4.** Small-scale array with 45 sample containers located in five heating blocks coupled to the heated manifold. The nine left-hand containers have the lids in place, yet do not have the gas sampling transfer lines connected.

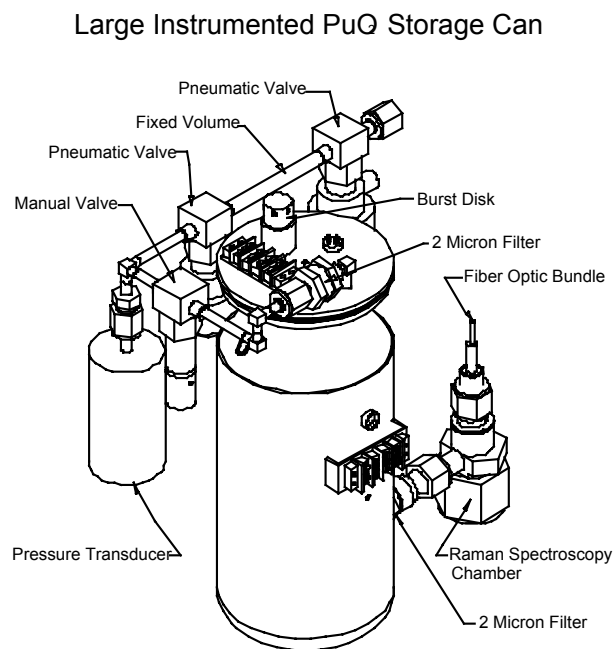
### ***Large-Scale Study Container Design.***

Multiple cans (9) containing up to 5 kg of material will be prepared for study. Materials will be sealed in BNFL inner containers that were designed to the DOE 3013 Standard. The cans are modified to accommodate fiber-optic probes, a gas sampling port, pressure and temperature sensors, acoustic resonance cell, and corrosion monitors. In order to minimize the effect of invasive gas sampling on the experiment, an effort is made to limit the gas sampling for gas chromatography / mass spectrometry to 10% of the total gas volume over the course of the experiment. The majority of the gas compositional data will be obtained through Raman spectroscopy. GC still remains a principal method because of its widespread acceptance as a gas analytical technique and its sensitivity to a wide range of gaseous species.

Figure 5 shows the container design assembly indicating key components. The design limits organic exposure to the oxide by minimizing the organic content of the parts and assembly components. The container and components are welded and subsequently leak tested. For several situations, epoxy was used to introduce feedthru wires. In these cases, the feedthru holes are drilled 0.001<sup>th</sup> of an inch larger than the wires and potted with epoxy on the exterior of the container.

Three modified containers have been prepared to date for the experiments: two experimental blank cans and the first oxide can (Can 1). The containers were received from Rocky Flats Environmental Technology Site (RFETS) and have a unique bar code number on the stainless steel. These numbers will be used for container identification. Figure 6 shows the modifications for two containers. The first oxide container will have

up to 10 thermocouples in a linear array so that information on  $\text{PuO}_2$  thermal conductivity can be obtained.



**Figure 5.** Full-scale can assembly indicating the design major components.



**Figure 6.** Modified experimental containers for one blank container, R200155, (left hand image) and the first oxide container R200145 (right hand image).

The modified lid is welded to the container inside the glove box by NMT-15 personnel after the material to be studied has been transferred to the container. The modified lid is



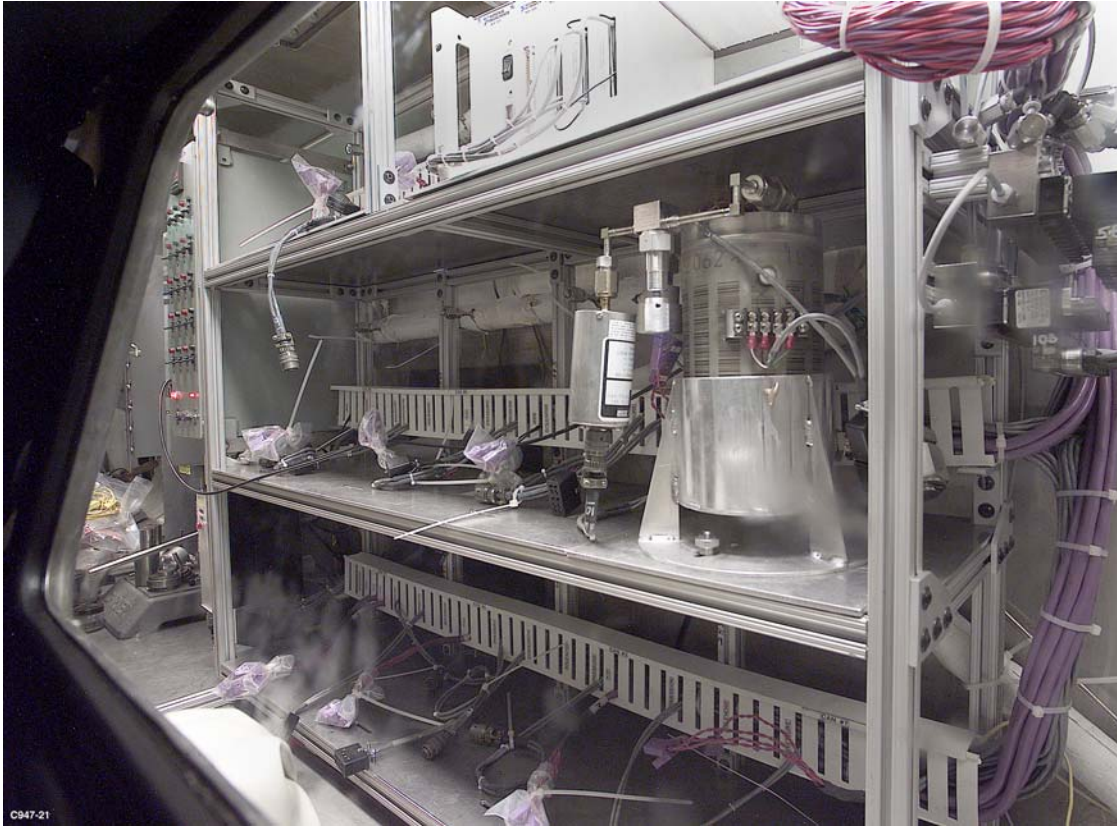
designed with a burst disk for pressure release in the event of an unexpected scenario of an  $\text{H}_2\text{-O}_2$  deflagration within the container. The burst disk is a passive safety-significant design feature for these containers and consists of a one-inch burst diaphragm with a 7/8 inch free flow diameter located in the lid of the container. The design of the lid for the containers with the burst disk unit in place is shown in Figure 5.

A rack system to hold the array has been designed, fabricated and tested (Figure 7). It contains a heated gas-manifold to minimize the effect of gas condensation enabling quantitative GC analysis. A wiring harness was fabricated for the remote monitoring of the pressure and temperature sensors and the automated control of the gas-sampling valves. All data acquisition instruments will be controlled remotely so that little or no manipulation in the glove box gloves will be required once the cans are in place.



**Figure 7.** Surveillance Rack for large-scale containers prior to installation inside a plutonium glove box. The rack will hold 10 containers, nine that will be loaded with oxide and one blank.

The Surveillance Rack was tested with containers and monitoring equipment in a non-radioactive environment. After the acceptance testing, the equipment was installed in the glove box during the third quarter of the fiscal year, Figure 8. Results from the non-radioactive and glove box testing are discussed below.



**Figure 8.** Surveillance Rack installed in a glove box with the first calibration can in location.

### **Large Scale Study Work Authorization.**

The Work Authorization for the large-can array is extensive for operation in PF-4. The Hazard Control Plan has been finalized [NMT-11-HCP-008.RO] for surveillance of 3013 containers in PF-4. Additionally, the work instruction for process operations has been completed and a second revision is underway. [NMT-11-WI-009.RO]

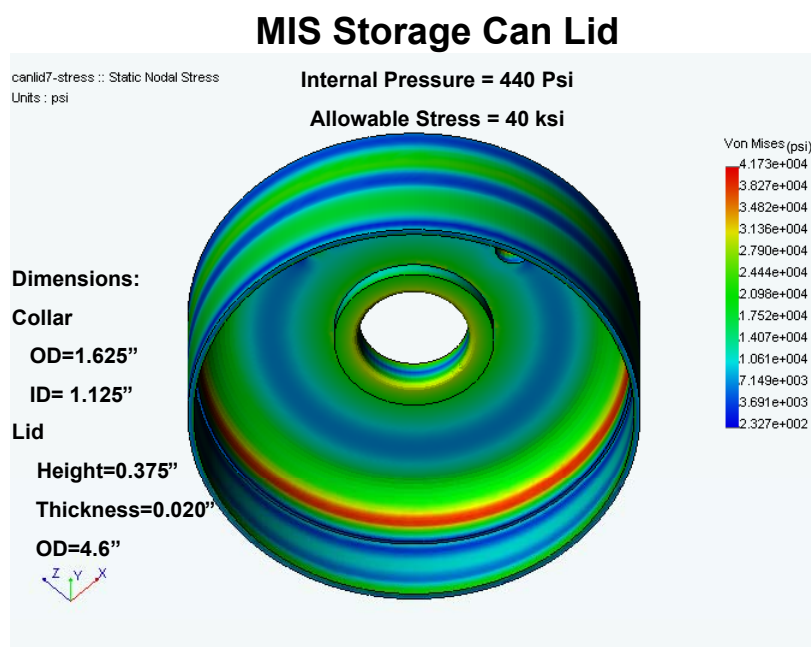
The Criticality Assessment has been completed [ESH-6-99-064, ESH-6-99-083, ESH-6-00-016]. Following a defense in depth approach, a recommendation was made that no more than 2 cans containing plutonium oxide could be handled outside of the Surveillance Rack at one time. The Nuclear Materials Control and Accountability (MC&A) program has written a variance for the containers [NMT4-00-058] requiring the following: a two person rule for the container loading, bolted containers in the Surveillance Rack, all openings fitted with a welded 2-micron filter, and acquisition of pressure / temperature data every 15 minutes. Following these requirements, the cans will be able to stay in the array and not have to be removed for periodic nuclear material inventory.

An ALARA (as low as reasonably achievable) assessment has been completed, indicating that shielding will be required when several containers are in the Surveillance Rack [ESH-12-00-22]. The shielding design has been completed and approved, the materials have been purchased and fabrication has recently been initiated. The recommendation by ESH-1 is to have the shielding in place by the time the third container is installed in the rack.



Frequent radiation monitoring will be done by ESH-1 to assure that ALARA conditions are met.

Structural analysis of the large container was completed to support the work authorization documentation. The container assembly with our modified welded lid containing the burst disk for pressure relief was modeled. The analysis of the assembly revealed a maximum allowable working pressure (MAWP) of 184 psig [ESA-EPE-01-132] for static use. It was also determined from ASME Boiler and Pressure Vessel Code Section III that a single-use application (where fatigue is not an issue) yields a maximum allowable pressure of 440 psig. Figure 9 shows the calculated von Mises stress distribution for the canister lid with a 440 psig internal pressure. The maximum stress occurs at the radius of the lid, a beneficial location that is removed from the lid penetrations.



**Figure 9.** Calculated stresses in the lid of the can assembly including lid penetrations.

The simultaneous presence of hydrogen and oxygen within the storage container headspace can lead to an additional pressure rise if a combustible hydrogen-oxygen mixture were to ignite. Additionally, calculations of H<sub>2</sub>-O<sub>2</sub> deflagrations at initial pressures of 130 psi (burst disk rupture pressure) made by Moody using Chemkin show pressure ratios as high as 10.9 for stoichiometric mixtures. [Moody 2001] This scenario, which is not expected to occur in the experiments, requires a 125-psig burst disk to be installed in the container lid [ESA-EPE-01-132, ESA-EPE-00-067, ESA-EPE-00-117 and ESA-EPE-00-138] with a free-flow diameter greater than 7/8 inch. The burst disk was also identified as a safety-significant feature that will be added to the TA-55 Technical Safety Requirements as a passive design feature. Administrative Controls for container

venting to ensure safety are also in place [NMT-11-WI-009] in the event that a container approaches 125 psig.

The Process Hazard Analysis has been completed [HA 2000] and it resulted in a positive Unreviewed Safety Question Determination (USQD) for eight of the ten containers. The HA is currently being reviewed by the DOE Los Alamos Area Office. A negative USQD was [USQ 2001] approved for the empty blank containers and the first container “Can 1.” The positive USQD for the remaining eight containers defines the project as a new experiment in PF-4 involving a Category 2 quantity of material. [USQ 2000] This outcome requires a Readiness Assessment (RA) prior to PF-4 work authorization. A limited scope RA Plan of Action [POA 2001] has been finalized for the large-scale surveillance experiments. The RA emphasis is on controlling hazards and reducing risks and will only focus on operations associated with pressurized systems, flammable gases and glove box operations involving large quantities of fissile material. The plan of action requires that the RA be demonstrated on the first oxide filled container, which is designed to be a baseline container that will not generate pressure [POA 2001]. It is expected that the first container will be loaded, installed in the surveillance rack and data acquisition initiated in the 2001 calendar year. The performance-based RA will be initiated following the experimental validation of the initial oxide can.

### **Gas Analysis.**

Significant work has been accomplished on the analysis methodology and results are presented below. Both the large and small containers are monitored for pressure and temperature continuously (multiple times an hour). For the large containers, the primary method of sampling is with Raman spectroscopy. During the course of the fiscal year, the Raman system was fabricated and tested. A sensitivity limit on the order of 0.5 Torr has been demonstrated for most gases [Berg 2001]. All data acquisition instruments will be controlled remotely so that little or no manipulation in the gloves will be required once the cans are in place. The project held an internal review early in the project, which led to a modification in the intrusive gas sampling instrumentation. Gas sampling by a mass spectrometer was previously planned for both the large- and small-scale experiments. Due to inherent difficulties in obtaining quantitative data, a change to quantitative gas sampling with gas chromatography was recommended and subsequently pursued. GC offers a robust design, quantitative analysis, enhanced data quality (mass spectroscopy peak overlap from N<sub>2</sub> and CO is eliminated) and high QA/QC standards. In the event that unidentified/unknown peaks are observed with the GC, a mass spectra will be obtained to identify the unknown component. The mass spectrometer can also be used to identify gas leaks in the system if necessary.

### ***Pressure and Temperature Measurements.***

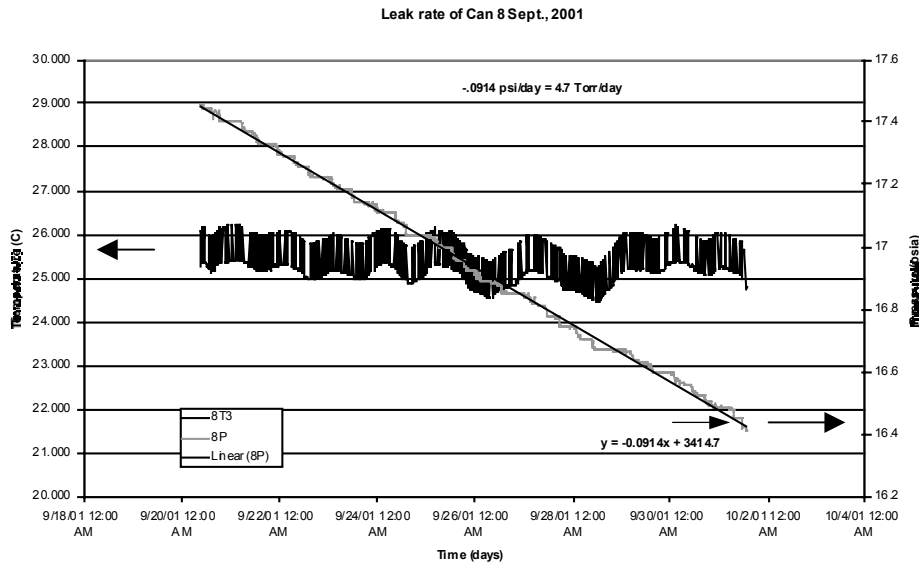
In verification and acceptance testing of the glove box installed equipment, two empty large-scale 3013 containers are installed in the glove box Surveillance Rack [T002062 and R200146]. The containers were filled with calibrated gas mixtures, and the

temperature and pressure have been monitored continuously at 15-minute intervals. [Veirs 2001 b] Demonstration of continuous monitoring supports the MC&A variance. Additionally, analysis of the temperature and pressure data allows a maximum leak-rate to be determined. Originally, leak checking was intended to be conducted shortly after the NMT-15 welding, yet due to loss of their leak checking capability, a leak checking methodology was developed for this project (see below under issues).

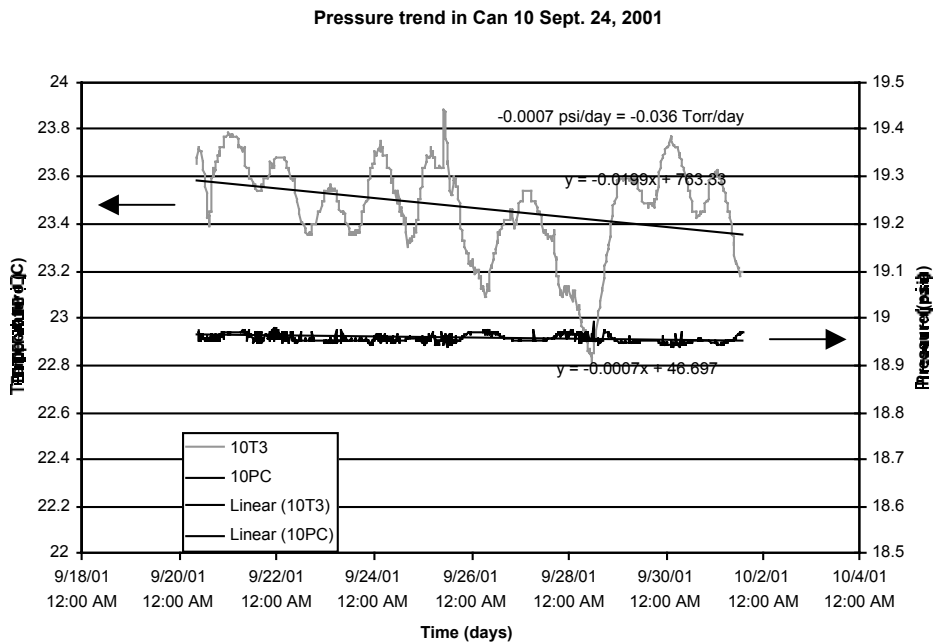
The large-scale container T002062, was the first demonstration of a modified container inside the glove box. After the lid was welded to the container, gas leaks were identified in the components separate from the lid weld. This forced the development of project specific leak checking and repair capabilities, and a requirement that all components be leak checked prior to introduction into the glove box. The leaks were repaired with Torr-Seal and the container (placed in position 8 in the Surveillance Rack) was filled with a calibration gas at approximately 17.5 psia. For the second empty blank container, R200146, the components were helium leak-checked prior to introduction into the glove box system and no leaks were found. The lid was welded as before and visual inspection of the weld showed a high-quality weld. The unit was evacuated in the staging glove box and monitored over four days. No leak was observed. The container was placed in position 10 in the Surveillance Rack and filled with a second calibration gas to approximately 19 psia.

The pressure and temperature monitoring results for T002063, Figure 10, indicate a leak rate of approximately 4.7 Torr/day. Due to the leak repair with Torr-Seal inside the glove box, it is no surprise that this container has leaks. Clearly, leak rates of this magnitude are easily detected over a day or two time frame. Filling a container with an overpressure of helium and monitoring the container over the usual three day weekend will readily allow detection of leaks of this magnitude.

The container in position 10 (R200146) behaved quite differently, Figure 11. Because there were two well-behaved thermocouples in this container, the pressure readings were corrected for temperature fluctuations by multiplying by the ratio of an average temperature and the temperature of the current reading. The pressure reading from this container is much more stable. The slope indicates a leak rate on the order of 0.04 Torr/day. This leak rate would result in a loss of 73 Torr or 1.5 psia over the course of five years. In order to observe this magnitude of leak rate with the quality of data we currently have, observations should be made for about one week. The temperature correction to the pressure does not completely remove the fluctuations due to temperature. Therefore, the trends in the temperature are still reflected in the pressure. The slope of the temperature data, if translated to pressure, corresponds to a pressure decrease of 0.06 Torr/day. The data indicate that this container may have no detectable leak at all.



**Figure 10.** Temperature and pressure data for the empty container, T002062, in position 8 on the Surveillance Rack inside the glove box. The temperature variation that is observed of +0.8 degrees up and down arises from the data acquisition reading open circuits in channels adjacent to the thermocouple being read in the system. This digital noise has been corrected for future measurements.



**Figure 11.** Temperature and pressure data for the second empty container, R200146, in position 10 on the Surveillance Rack inside the glove box.

In order to have reliable leak-checking data, the cans must be filled with an overpressure of around 20 psia of helium and monitored for a week. A leak rate of 0.04 Torr / day from these containers is equivalent to approximately  $2 \times 10^{-6} \text{ cm}^3/\text{sec}$ . After a week, the pressure will be reduced to the working pressure for that container.

### ***Gas Chromatography Results..***

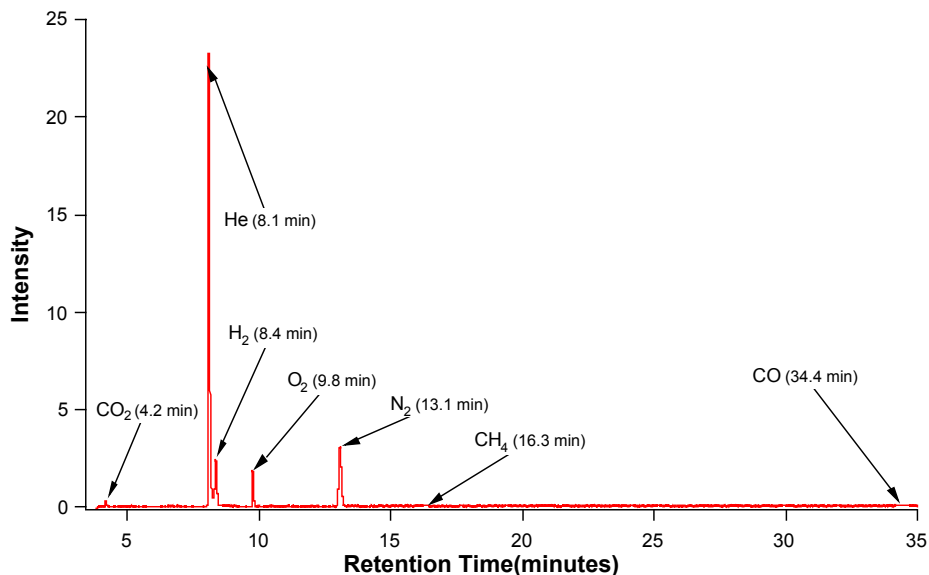
As discussed above, GC sampling will be done periodically to confirm Raman spectroscopy results and offer a quantitative check on the gas constituents for the large containers. It will also be able to detect most monatomic gases (He, Ne, but not Argon) that Raman spectroscopy is unable to detect. GC will also be the primary analysis method for the small containers where only periodic gas sampling will be done so that less than 10% of the total gas volume will be removed during the course of the experiment. In the large-scale study, the GC samples are collected remotely by air-actuated valves driven by the data acquisition system. This allows for both a reduction in radiation exposure and human error during the sample collection.

GC measurements have been taken for various calibration mixtures that include gas components that may be observed during the course of the experiments. Table 1 and Figure 12 show the gas sample composition and GC spectra, respectively, that were taken during the non-radioactive test phase of the large containers. Subsequent sampling and error analysis has identified several factors that limit the accuracy and sensitivity of the large-scale container GC measurement. [Harradine 2001] In considering these factors, it is expected that the current configuration allows a gas determination of  $1.2 \pm 1$  Torr partial pressure in the container.

**Table 1.** Concentration of gas components in the calibration gas.

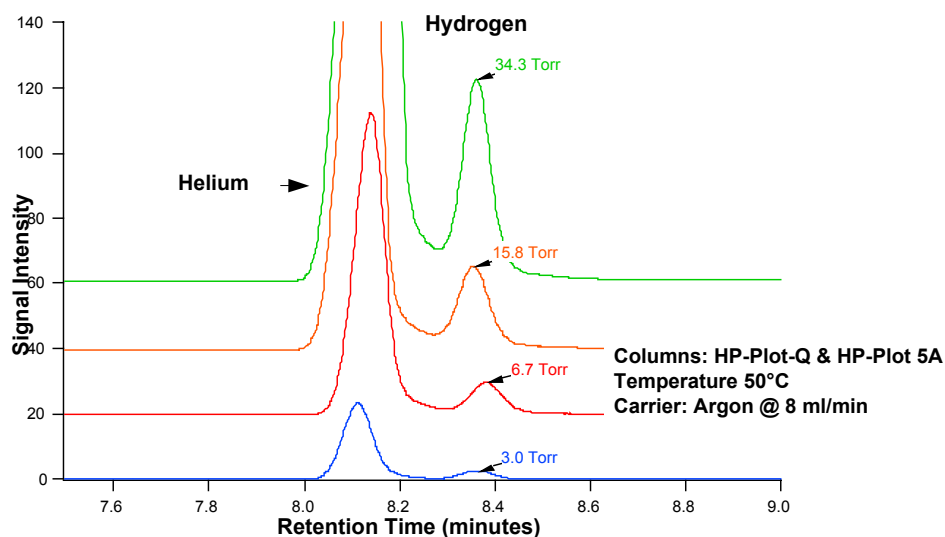
<b>Component</b>	<b>Volume %</b>	<b>Partial Pressure (Torr)</b>
CO <sub>2</sub>	5.03	3.77
He	71.99	53.99
H <sub>2</sub>	4.04	3.03
O <sub>2</sub>	4.97	3.73
N <sub>2</sub>	4.98	3.74
CH <sub>4</sub>	4.00	3.00
CO	4.99	3.74





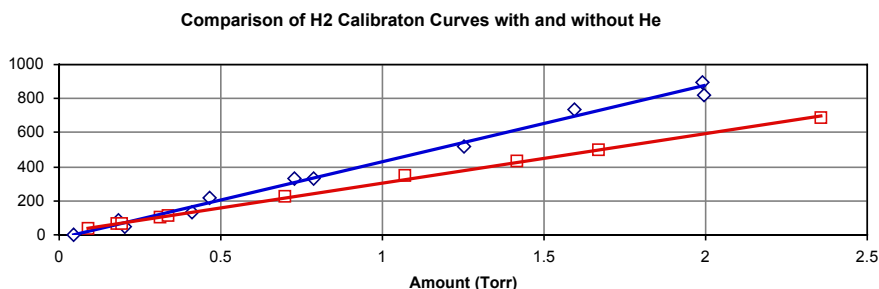
**Figure 12.** Gas chromatography spectra collected from a large-scale surveillance container showing sensitivity to the gases in the calibration mixture.

Figure 13 shows a series of GC spectra obtained at different gas pressures illustrating the hydrogen sensitivity. We have also obtained similar GC from instrumented containers inside the plutonium glove box. Additionally, multipoint calibration curves have been obtained for each gas component in the large-scale containers in glove box. For quality control, a single point calibration will be taken prior to each day a can or series of cans are to be samples. If the data falls on the multipoint calibration curve, no further action is necessary. [Harradine 2001]



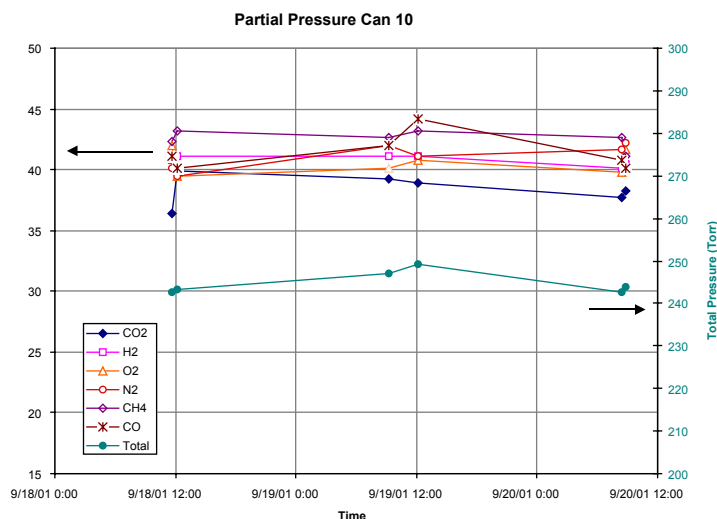
**Figure 13.** Gas chromatography results showing the partial pressure of hydrogen observed in a blank storage container using the calibration gas mixture.

As indicated in Figure 13, the retention time for hydrogen and helium can overlap and subsequently cause interference with the hydrogen quantitative analysis. Because helium will be the fill gas in some of the large-scale containers and many of the small-scale containers, we established two different calibration curves for hydrogen depending on whether or not helium is the majority gas in the container headspace. Figure 14 compares the two calibrations. The calibrations of the other constituents are unaffected.



**Figure 14.** Gas chromatography results for hydrogen calibrations. Two different calibrations are obtained depending on whether the container is filled with helium or air.

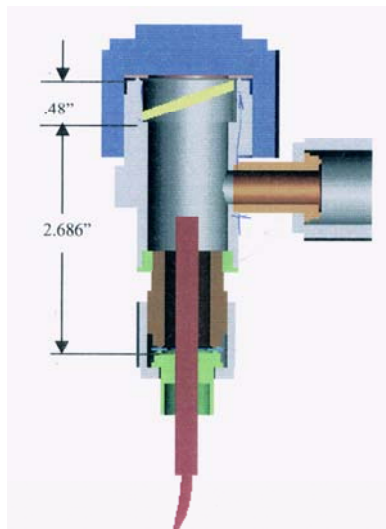
One primary for monitoring a storage can containing only a calibration gas is to determine the reactivity of the various species with the stainless steel walls. Figure 15 shows the partial pressures of the various species of a calibration gas in a large-scale container (R200146) over a two day period. No particular trend is seen indicating that on this time scale little reaction with the can walls is occurring. Assuming no wall reactions the run to run variation in the measurement is no worse than 2 Torr (for CO) and no better than 0.8 Torr ( $H_2$ ) twice the standard deviation of the measurement and is consistent with the  $\pm 1$  Torr accuracy stated above.



**Figure 15.** GC sampling variation and gas mixture reactivity in large-scale container R200146.

### ***Raman Spectroscopy Results***

The design of a Raman collection chamber was completed, integrated into the large-scale container (Figure 5) and tested. Gases are detected within an enclosure without sample removal or pre-concentration. The chamber contains an unfiltered, non-imaging fiber-optic probe and a black, colored glass filter tilted to direct reflections away from the probe tip. The design is shown in Figure 16. The fiber-optic probe head consists of a fiber-optic bundle with one center excitation optical fiber and six surrounding collection optical fibers. The container is isolated from the oxide material by a 2 micron filter.

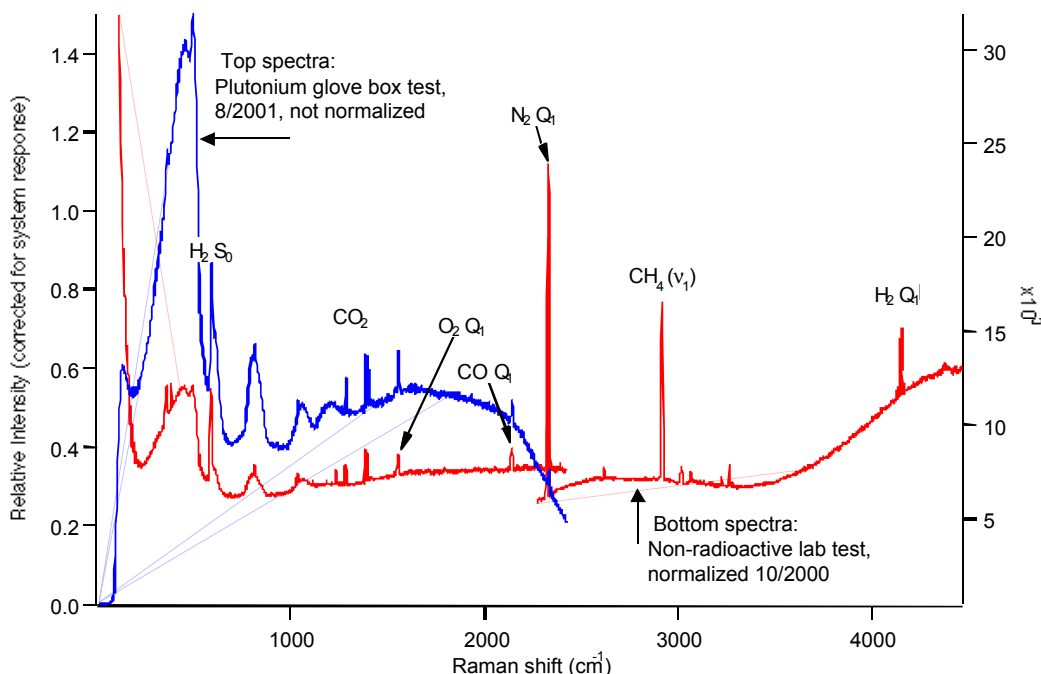


**Figure 16.** Cross sectional view of the Raman chamber. The fiber-optic bundle enters the chamber from the bottom and the chamber is attached to the experimental can from the side. The scattered light is reflected away from the probe head by a tilted glass filter at the top of the chamber.

The initial Raman measurements of relative gas composition within the large-scale cans are discussed below. Spectra were collected in sealed containers located in both a non-radioactive laboratory and in a plutonium glove box. A typical Raman spectrum obtained with the above configuration is shown in Figure 17. This spectrum, which was obtained in the glove box, was not normalized and only collected to  $\sim 2400 \text{ cm}^{-1}$ .

Raman spectra of gas mixtures exhibit distinct scattering peaks characteristic of each gas present in the sample (excluding monatomic gases such as He and Ar). Peak areas are proportional to gas concentration, with the proportionality factor being dependent on the gas and on the instrumentation.

In order to compensate for most of the possible variation of the proportionality factors due to changes in instrumentation, peak areas can be compared to an internal standard within the sample being measured. The ratios of the proportionality factor of the gas to be measured and the internal standard can be determined by measuring a known gas mixture. These ratios can then be used to determine unknown gas concentrations of mixtures containing the internal standard at a known concentration.



**Figure 17.** Raman spectra of calibration gas mixture obtained from large-scale containers located in a plutonium glove box (top spectra) and in a non-radioactive laboratory (bottom full spectra). Data acquisition is typically done with less than 0.5 watts of 532 nm light for 1200 seconds of integration time. The peak assignments are labeled in the spectrum.

The method was tested on a calibration gas mixture of known concentration in a can within a glove box. Five Raman spectra were acquired from the can over three days. The Raman peaks in each spectrum were integrated without any prior processing of the data. Area-to-pressure proportionality factors were determined for each peak using the known composition. The ratios of these factors to that of the nitrogen  $Q_1$  peak in the same spectrum were calculated.

The current plan is to introduce a small, known amount of nitrogen into future cans containing  $\text{PuO}_2$ . This will serve as an internal calibration standard for the Raman spectra to supplement the external calibration from the GC results. Other gas pressures will be calculated by multiplying the measured ratio of their peak areas to that of nitrogen peak and by the proportionality factors determined from the can containing the calibration gas.

The uncertainties that will exist in the calculated gas pressures can be partially estimated by characterizing the distributions of the ratios of various gas peak areas to the nitrogen peak area in the five spectra of the calibration gas that have been taken so far.

The tabulated results, Table 2, show that raw peak areas varied with a standard deviation of between 8 and 15% over the five runs. Variation in peak areas relative to that of nitrogen were more stable, varying by 5% or less with the exception of the higher-energy of the two  $\text{CO}_2$  peaks. This translates into a pressure uncertainty of 2 Torr out of 40 Torr for most gases in the calibration mixture when using nitrogen as an internal standard.

**Table 2.** Summary of mean and standard deviation of peak areas in five Raman spectra of known gas mixture. The known partial pressures are shown, along with the relative standard deviation of the peak area ratios expressed as a percentage and as a pressure.

<i>Gas</i>	<i>Mean Raman peak area (5 measurements)</i>	<i>Standard deviation of area measurements (%)</i>	<i>Actual pressure (Torr)</i>	<i>Standard deviation of measured pressure (Torr)</i>	<i>Relative standard deviation of pressure (%)</i>	<i>Error in pressure in Blank Can 2 (%)</i>
N <sub>2</sub>	32,200	9.9	39.39	N/A	N/A	
CO	41,800	11.1	39.78	2.0	4.9	-1.0
O <sub>2</sub>	65,600	10.1	39.19	1.2	3.0	3.6
CO <sub>2</sub>	80,200	14.5	38.90	3.8	9.7	31.3
CO <sub>2</sub>	49,600	8.8	38.90	2.0	5.2	-0.3
H <sub>2</sub>	156,200	11.7	38.61	1.5	3.8	-4.5

The lower uncertainties in the areas result from intrinsic compensation by the internal standard for most forms of alignment drift in the excitation and collection legs of the Raman system. An internal standard also compensates for inevitable differences in efficiency between fiber-optic Raman probes used on different cans. A second can (Blank Can 2) was filled with the same calibration gas mixture and interrogated with a different fiber-optic probe. The final column of Table 2 shows the relative errors in the partial pressures of gas components determined from the ratios of the peak areas to nitrogen and the constants of proportionality determined from the first. The two cans were interrogated six weeks apart. The errors remain below 5%, with the exception of one CO<sub>2</sub> peak where the sporadic, random noise from cosmic rays coincided with the peak and made accurate integration impossible. This would normally be addressed by acquiring multiple spectra and discarding large outliers.

***Raman and Gas Chromatography Comparative Results: Oxygen diffusion from Raman chamber into oxide filled container.***

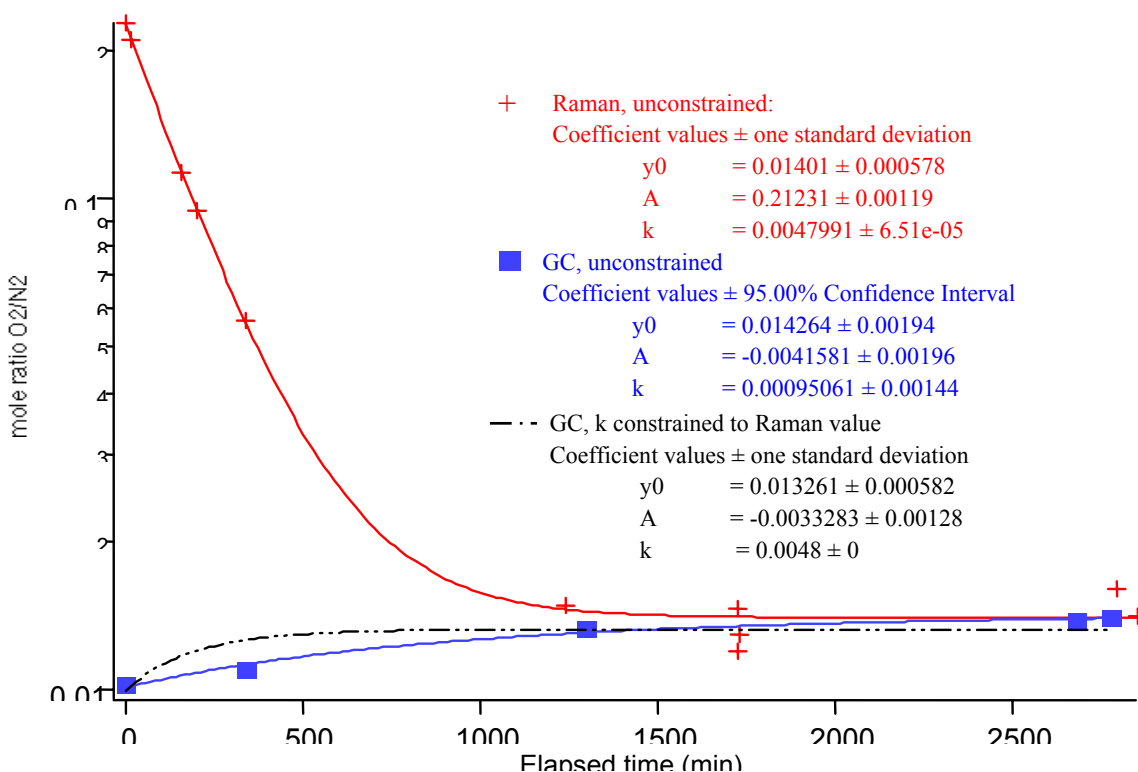
The design of the large-scale container includes measurements of the gas composition from both the top and the bottom of the container from Raman and GC analysis, respectively. An initial concern raised by the MIS Working Group was the time for equilibrium to be reached between the two sampling locations following a rapid change in gas composition. If the equilibrium time were too long, the gas sampling results would not be comparable.

During non-radioactive testing, gas diffusion measurements were made on a sealed container filled with CeO<sub>2</sub>. The CeO<sub>2</sub> served as a PuO<sub>2</sub> surrogate. The sealed container was prepared with gas exchanges and humidification without the Raman chamber attached. It was then moved to the surveillance rack and the electrical and piping connections were made. A Raman chamber of an original, larger design, and containing ambient air, was attached to the lower fitting on the side of the can. The time from



removal of the cap on the container fitting to sealing of the Raman chamber was approximately three minutes.

After the attachment of the Raman chamber, data acquisition was begun with both the GC and Raman and continued intermittently for 48 hours. The nitrogen and oxygen peak areas were measured by the native GC peak fitting routine and were fit by single gaussians with no parameter constraints and a cubic baseline for Raman. The areas were then converted to partial pressure ratios of oxygen to nitrogen using measurements on ambient air as a calibration. Finally, the results were plotted versus elapsed time (minutes) from the first data acquisition, Figure 18. Note that this is not a true  $t_0$  for the initiation of air diffusion because the delay from the attachment of the Raman chamber to the initial data acquisition was not recorded. This is reflected in the fitted Raman data in that the value of  $A$  would be 0.268 if the sample in the Raman chamber was ambient air at  $t=0$ . From the exponential fit and the time concentration ratio in air, we calculate the time lapse from the attachment of the chamber to the initial data acquisition to have been 37 minutes. This is in reasonable agreement with our unrecorded recollection of the time sequence.



**Figure 18.** Curve fits of Raman (+) and GC (■) data from diffusion of  $O_2$  from the Raman chamber into the oxide filled container.

The diffusion data, shown in Figure 18, was fit with the exponential equation  $y = y_0 + A \exp(-k \cdot t)$ . The curve fits are included in the figure. The rate constants determined from the unconstrained fits were  $1/k = 208$  and  $1051$  minutes for the Raman and the GC

measurements, respectively. If the GC data is fit with a constrained Raman  $k$  value, then the dashed curve is predicted, which does not go through the observed data. The unconstrained GC fit of  $1/k = 1051$  minutes is considered a real observable. The diffusion of the gas from the Raman chamber, located near the bottom of the can, through the oxide interstitial spaces to the headspace area takes longer than mixing the gas in the Raman chamber with the gas in the interstitial spaces of the oxide. From these results, we conservatively assume that gas equilibrium is reached within 18 hours after the Raman chamber is attached.

### **Large-Scale Staging Area.**

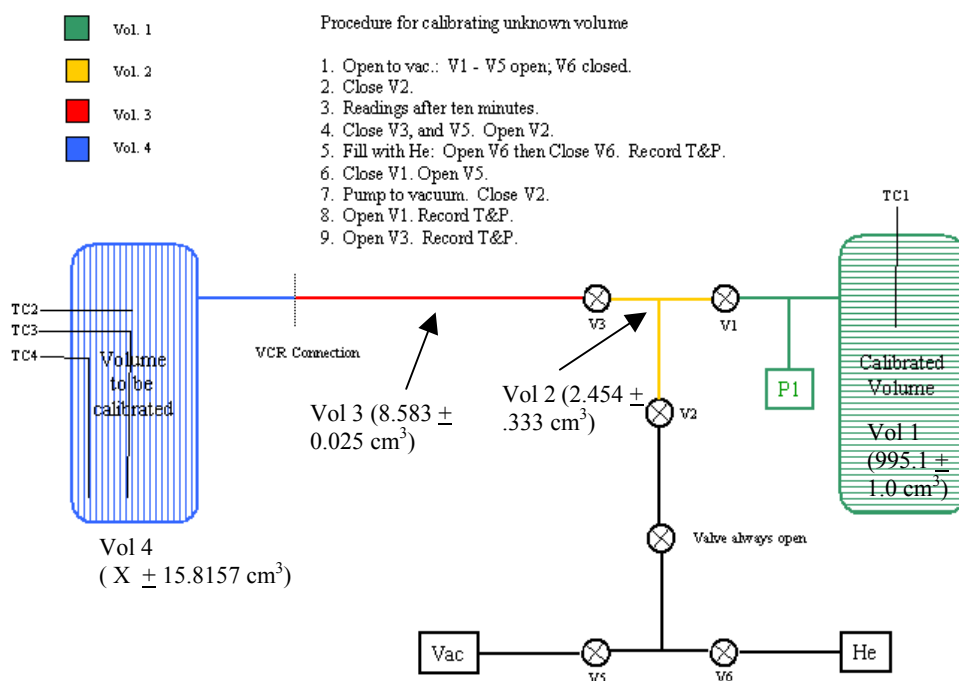
Oxide material is loaded into a large-scale container in the staging glove box. The container is welded shut by ARIES personnel and subsequently sent for calorimetry analysis for plutonium accountability verification. The container is prepared for the surveillance rack by a sequence of steps that include leak checking, volume calibration, and gas exchange.

The measurement of the internal volume and volume calibration of the large containers is done by a volume expansion method. [Veirs 2001a] The schematic of the experimental set up is shown in Figure 19. Figure 20 shows the balance and calibrated volume for container preparation installed inside the glove box.

The volume of the calibrated container was determined by measuring the mass gain and temperature when filled with de-ionized water. The other volumes were calculated by gas expansion from the calibrated volume. Errors in the system were also determined which allows a final uncertainty for the volume of the large-scale container to be  $15.8 \text{ cm}^3$ .

The volume of 2 large-scale containers (the first 2 blank empty containers) was determined. The results are summarized in Table 3. The volume of the modified large-scale containers calculated from the dimensions of the machined pieces is  $2276 \text{ cm}^3$ . This can be compared to the values reported in Table 3. The agreement is within the uncertainty. Modifications have been suggested to improve the errors and procedure for volume calibration. The modifications are currently being implemented. [Veirs 2001a]

In four containers moisture is added by flowing a humid gas through the oxide. The moisture content of the oxide is monitored by the weight gain over time with a data acquisition system. Figure 21 shows the glove box staging area.



**Figure 19.** Schematic of equipment used to determine the internal volume of MIS containers. P1 is a 1000 Torr Baratron head, TC1 is a Type K thermocouple, and TC2-4 are Type E thermocouples. Data are read off of the MKS readout and thermocouple readout.

**Table 3.** Volumes and uncertainties in determination of the large scale container volumes.

	Volume (cm <sup>3</sup> )	2 $\sigma$ (cm <sup>3</sup> )
Volume 1	995.1	1.0
Volume 2	2.5	0.4
Volume 3	8.6	0.4
Can R200146	2271	16
Can T002062	2287	16



**Figure 20.** Balance and calibrated volume for container preparation inside the large-scale container staging box.

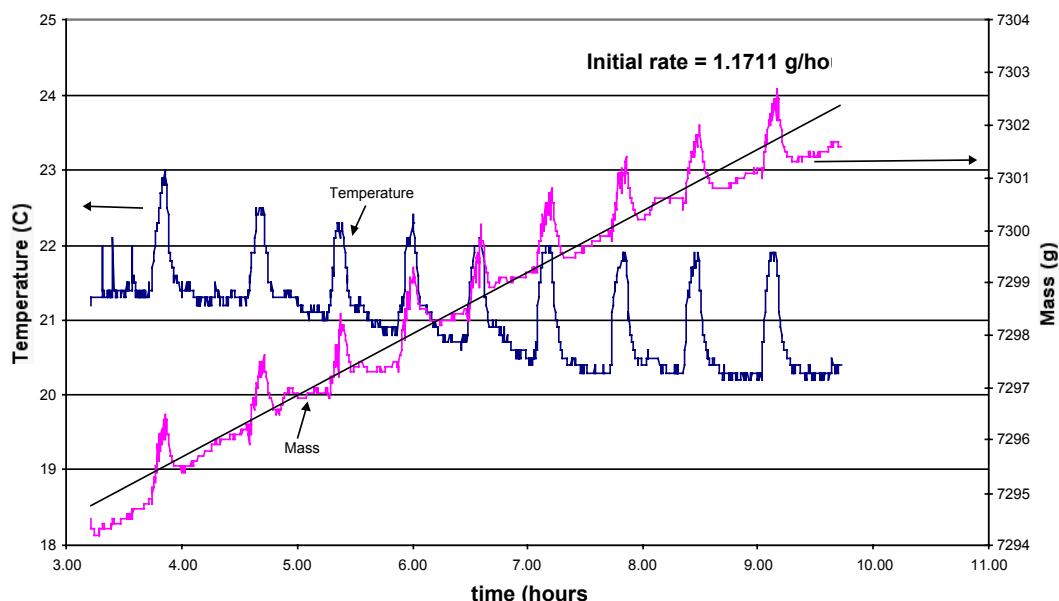


**Figure 21.** Glove box staging area for large-scale containers. The humidity generator, pumping and control stations are located under the glove box.

### ***Moisture adsorption on $CeO_2$***

A series of non-radioactive room temperature tests were conducted to assess the humidification and gas exchange equipment.

A full-scale container was filled with  $\text{CeO}_2$  (3300 grams) and welded shut. Prior to this, the  $\text{CeO}_2$  was dried for three hours at  $400^\circ\text{C}$ , where 13.1 grams of mass was lost. The sealed container was placed on the balance and connected to the calibrated volume shown in Figure 19. Humid gas (60% relative humidity of  $\text{N}_2$  gas) was introduced at 6 SCFH into the container through the bottom port where the Raman chamber attaches. The humid gas flowed through the oxide and exits the top port where the pressure transducer and GC sample manifold attaches. The temperature, humidity and mass were recorded continuously. The experiment was conducted in two stages for a total of 22.8 hours. The mass gain during the first stage is shown in Figure 22.



**Figure 22.** Mass gain of  $\text{CeO}_2$  when exposed to 60% relative humidity gas (6 SCFH  $\text{N}_2$ ) for the initial ten hours. The line is a fit through the mass data as a function of time. The temperature data is also included and shows the temperature fluctuations due to the air conditioning cycling in the non-radioactive laboratory.

A linear fit through the mass gain data indicates an initial moisture uptake rate of 1.17 grams water / hour for the oxide. It is noted that the data is not linear: at early times a faster rate is observed, and at longer times a slower rate is observed. During the second 12 hours, an ending rate of 0.36 grams water/ hour was determined. After 23 hours, no further weight gain was observed. During the course of the experiment, a total of 13 grams of water was adsorbed onto the oxide.

The results (Table 4) are consistent with a plutonium oxide moisture uptake model [Veirs 2000] where the moisture uptake is dependent on the specific surface area of the oxide. The  $\text{CeO}_2$  used in this experiment had a specific surface area of  $3.84 \text{ m}^2/\text{g}$ . The 13 grams of added moisture corresponds to 4.7 monolayer equivalents of water adsorbed on the surface. Heating the material initially to  $400^\circ\text{C}$  drove off these water layers, resulting in a



loss of 13.1 grams of water. It is assumed that the heat treatment did not drive off the hydroxide layer bound directly to the oxide surface, which is believed to be removed at much higher temperatures.

The rate uptake results indicate three different rates of adsorption. One rate is observed during the first few hours, which is taken to be the adsorption of the first monolayer equivalent of water. The second rate of 1.17 grams / hour can be attributed to additional monolayer (2-4) equivalents of water adsorbing on the surface. The final slower rate is indicative of the material approaching equilibrium and represents the adsorption of the final higher layers of water. Similar results are expected to be found with pure plutonium oxide.

**Table 4.** Moisture uptake results for CeO<sub>2</sub>

<b>Monolayer equivalents adsorbed</b>		
Mass of CeO <sub>2</sub>	3300	g
specific surface area of CeO <sub>2</sub>	3.84	m <sup>2</sup> /g
Total surface area	12672	m <sup>2</sup>
Mass of water in one monolayer (using 0.22 mg/m <sup>2</sup> ) [Haschke 1995]	2.8	g
Monolayer equivalents adsorbed	4.7	monolayers

### **Oxide Materials.**

Oxide materials representing inventories destined for long-term storage throughout the DOE complex will be monitored. Thirty-three items from Hanford and Rocky Flats Environmental Technology Site have been evaluated by the LANL MIS project. [Mason 1999] Residuals from these evaluated items make up the surveillance items to date. In the future, materials may be drawn from the Los Alamos inventory or from other sites to assure that these inventories are represented for safe storage under the 3013 standard. The materials will be characterized as necessary prior to packaging in the large- or small-scale containers. Characterization data will include density, isotopics, particle size, specific surface area, moisture content (via neutron moderation, LOI and supercritical fluid extraction), wattage, and chemical composition.

### ***Small-Scale Materials.***

The small 10-gram samples will allow a database of many material types prepared for storage in various ways and in contact with various gases to be compiled. [Worl 2001d] For the initial small-scale study, forty-five containers are planned. Forty will contain oxide material, and 5 will contain experimental blanks. The capacity can be increased to 90 containers dependent on the complex-wide needs. The 5 x 9 container array is designed so that 5 independent temperatures can be set for each row of nine small-scale containers.

The selection of the samples will be done with cooperation with the MIS working group. A draft Sample Selection Plan has been proposed [Worl 2001d]. These samples will be selected to address known existing uncertainties in gas generation and safety considerations associated with specific material types being considered for storage. They will also contain samples of the actual materials going into the large-scale study and offer data validation with ongoing efforts. A percentage of the oxide materials in the small-scale study will be used for data validation of gas generation models in development across the DOE complex. Approximately half of the proposed small-scale samples meet the criteria in the 3013 standard (950°C, 2 hour calcination; >30wt.percent plutonium; <19 watts; and <0.5 wt. percent water).

From recent and earlier work, the effect of several material and packaging variables have been suggested that need further study to assure the safe storage of sealed containers with Pu materials. Each experimental variable (or set of variables) will address a specific previously identified question. For example, two identified variables that will be represented in the small-scale samples are water and salts in plutonium oxides. The question that will be addressed is the effect on pressure generation from potentially hygroscopic components in the oxide ( $\text{MgCl}_2$  or  $\text{CaCl}_2$ ). The selection criteria for the small-scale samples are based on exploring the relevant variables thoroughly and efficiently.

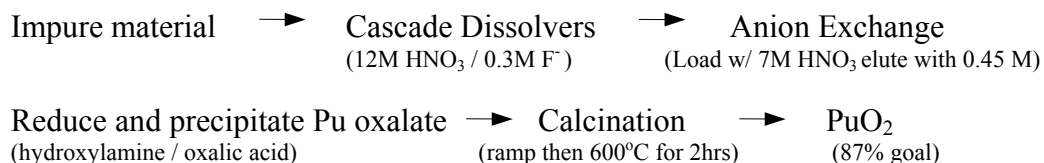
Initial start-up activities during the first six months include both experimental duplicates and blanks. After the initial six months the blanks and duplicates will be phased out and additional oxide samples will be loaded. One blank will reside in the matrix at all times. The experimental replicates will be done on two of the large-scale sample duplications. These results will verify experimental reproducibility and the reproducibility of the sample behavior. Four replicates will be done initially on each sample to provide quality assurance. After a short period of time (~six months) with consistent behavior, two of four samples will be removed and the remaining two will remain for monitoring as duplicates.

It is important to note that the proposed sample matrix is flexible and dependent on the MIS Working Group and site needs. It is also anticipated that an annual review of the data acquisition results will determine the termination of an experiment.

### ***Large-Scale Materials.***

Ten instrumented inner 3013 containers will be installed in PF-4 to establish compositional changes in gases over plutonium oxide materials for an extended time. Characterized oxide material, in nine of the containers, will be in varying forms (pure  $\text{PuO}_2$ , x%  $\text{H}_2\text{O}$ /  $\text{PuO}_2$ ,  $\text{PuO}_2$  with salt,  $\text{PuO}_2$  with other material (plastics), etc...). The tenth container will exist as an experimental blank. The material matrix (Table 5) encompasses bounding, safety-driven scenarios for long-term storage. The selected material for storage is based on iterative guidance from the MIS working group. Slight modifications have recently been approved as an outcome the MIS Working Group Meeting, October 17-19, 2000.

The oxide materials planned for the containers are listed in Table 5. The material will be obtained from the LANL Actinide Processing Group (NMT-2) who will prepare it from calcination following the oxalate precipitation process in the following sequence:



The typical characteristics of the material is 0.5-1.5 wt.% loss on ignition, 20 - 60 m<sup>2</sup>/gm specific surface area, 1.8 - 2.0 g/cm<sup>3</sup> loose powder density. The material will be prepared per the specifications listed in Table 5.

Several technical issues will be explored through the matrix array developed in Table 5. The first can (can 1) serves as the baseline and will be pure oxide packaged according to the 3013 Standard. The effect of the specific surface area (cans 1,2,3) will determine the effect of free water and gas generation on the oxide surface area. It has been proposed by Veirs [Veirs 2000] and others that in the case of high specific surface area, 0.5 wt. % water is bound tightly to the oxide in first few monolayers, thus no water can be found in the vapor phase. On the other hand, a low specific surface area oxide (1 m<sup>2</sup>/g) containing 0.5 wt. % contains approximately 20 water monolayers, of which about 18 are loosely bound, generating water in vapor phase. The effect of water on gas generation (cans 2,3,7,8) will be determined by the exposure of the oxides to a humid environment.

A critical corrosion issue within the cans will be addressed with the addition of chloride salts (cans 4,8) to oxide materials. The issue of HCl generation, corrosion, and low plutonium content (<50 wt.%) will be studied. The generation of H<sub>2</sub> and CO<sub>2</sub> gases will be explored with the addition of organics (cans 5,6) and moisture. This scenario may result in increased pressures. One can (can 7) will be heated to a higher temperature to mimic the possible SRS storage temperature generated inside a sealed can array with added solar heat. The effect of the fill gas (cans 1,4,5,6,8) will also be studied. If air is the fill gas, the back reaction of generated H<sub>2</sub> with oxygen from air may actually limit the H<sub>2</sub> production. And finally, a mixed oxide (can 9) will explore the effect of uranium oxide where U<sub>3</sub>O<sub>8</sub> may act as a H<sub>2</sub> sink and generate water. Details of the container contents are described below.

**Can 1.** The first can serves as the baseline and will be pure oxide packaged according to the 3013 Standard. The oxide described above will be calcined at 950°C for two hours, have a moisture content of <0.5 wt.%, and a specific surface area < 5 m<sup>2</sup>/g. The material will be sealed in a He atmosphere at ~570 Torr. The container will have an additional eight thermocouples placed in a linear array within the oxide so that thermal conductivity information will be obtained.

**Can 2.** The oxide will be a much higher surface area oxide, >10 m<sup>2</sup>/g and serves as a pure oxide prior to the 950°C calcination. The oxide will be exposed to a moist He gas so that a final moisture content is 0.5 wt.% water (upper 3013 standard limit). The gas flow will be stopped when 25 grams of H<sub>2</sub>O are added to the oxide or the oxide stops picking up water. The material will be sealed in a He atmosphere at ~570 Torr.

**Can 3.** The oxide will be prepared as Can 1. After the final calcination step the oxide will be exposed to humidity by allowing moist He gas to pass through the container. The water uptake will be monitored by weight gain. The gas flow will be stopped when no further weight gain occurs or 100 grams of H<sub>2</sub>O are added to the oxide. The material will be sealed in a He atmosphere at ~570 Torr.

**Can 4.** The oxide from the oxalate precipitation process will be blended with 33 wt% CaCl<sub>2</sub> and 33 wt% MgCl<sub>2</sub> salts. The oxide will simulate a low-grade Pu oxide with hygroscopic chloride salts. The material will be calcined at 600°C to simulate a low stabilization temperature or 3013 process upset. The final material will have some weight loss due to volatilization of the salts during calcination. The material will be sealed in a dry air atmosphere at ~570 Torr.

**Can 5.** The oxide from the oxalate precipitation process will be blended with 5 wt% polyethylene particles. The material will be calcined at 600°C to simulate a low stabilization temperature or 3013 process upset. The final material will have some weight loss due to pyrolysis of the plastics during calcination. The material will be sealed in He at ~570 Torr.

**Can 6.** This oxide will be identical to Can 5, but the material will be sealed in a dry air atmosphere at ~570 Torr.

**Can 7.** This container will simulate the off-normal temperature scenario analyzed at Savannah River Site. The material will be prepared as Can 3, and be exposed to a moist He gas so that a final moisture content is 0.1 wt.% water. The container will be insulated and heated if necessary to achieve an average gas temperature of 210°C. The gas flow will be stopped when 10 grams of H<sub>2</sub>O are added to the oxide. The water limitation of 10 grams will allow data acquisition without approaching the 125 psig rupture disk pressure due to water vapor pressure generated at an elevated temperature. The material will be sealed in a He atmosphere at ~570 Torr.

**Can 8.** The results will be comparable to Can 4. Data collected from Can 4 will be reviewed prior to the preparation of Can 8. The oxide will be blended with 33 wt% CaCl<sub>2</sub> and 33 wt% MgCl<sub>2</sub> salts. The oxide will simulate a low-grade Pu oxide with hygroscopic chloride salts. The material will be calcined to the 3013 Standard at 950°C for 2 hours. After the final calcination step the oxide will be exposed to humidity by allowing moist air gas to pass through the container. The water uptake will be monitored by weight gain. The gas flow will be stopped when no further weight gain occurs or 100 grams of H<sub>2</sub>O are added to the oxide. The material will be sealed in an air atmosphere at ~570 Torr.

**Can 9.** A mixed oxide with high uranium content will be prepared by blending prepared PuO<sub>2</sub> with U<sub>3</sub>O<sub>8</sub>. The material will be prepared according to the 3013 Standard, with 2 hours of 950°C calcination and a measured LOI of <0.5 wt.%. This oxide may also originate by blending actual MIS mixed oxide items together. This will depend on availability of the MIS items. The material will be sealed in a He atmosphere at ~570 Torr.

**Table 5.** Large-scale matrix of oxide material.

CAN	MATERIAL <sup>a</sup> (5 kg/ can) <sup>b</sup>	Composition	Pu oxide (g)	Fill Gas	COMMENTS
1	Pure PuO <sub>2</sub> , <sup>c</sup> calcined at 950 °C, final SA<5 m <sup>2</sup> /g, H <sub>2</sub> O<0.5wt%	5000 g PuO <sub>2</sub>	5000	Helium	Baseline - 3013 standard
2	"As Received," SA > 10 m <sup>2</sup> /g, prior to final calcination, 0.5% H <sub>2</sub> O (25 gms H <sub>2</sub> O)	5000 g PuO <sub>2</sub>	5000	Helium	Finely divided powder/ specific SA effect
3	same as 1 + 60% humidity for 1 week, (100 gms H <sub>2</sub> O, 2% cap)	5000 g PuO <sub>2</sub> + moisture added by humidity	5000	Helium	Effect of H <sub>2</sub> O on Low surface area (worst case of 1 and 2)
4	34% PuO <sub>2</sub> +33%MgCl <sub>2</sub> +33%CaCl <sub>2</sub> salt, 600°C calcination	1700 g PuO <sub>2</sub> / 1650 g CaCl <sub>2</sub> / 1650 g MgCl <sub>2</sub> mixture blended before calcination	1700	air	Impure, low stabilization temperature; Salt; corrosive gases; alot to be packaged
5	Pure PuO <sub>2</sub> + 5% organics calcined at 600°C	4750 g PuO <sub>2</sub> / 250 g PE, mixture blended before calcination	4750	Helium	Effect of organics; likely real problem
6	same as 5	4750 g PuO <sub>2</sub> / 250 g PE, mixture blended before calcination	4750	air	Does oxygen retard H <sub>2</sub> formation?
7	PuO <sub>2</sub> ,19W or external heat->250 °C storage T, 60% humidity for 1 wk so that 10 grams H <sub>2</sub> O (0.1% cap) is added	5000 g PuO <sub>2</sub> + moisture added by humidity	5000	Helium	Temperature effect
8	same as 4, calcined at 950 °C, then exposed to 60% humidity for 1 week- 2% H <sub>2</sub> O cap	4490 g PuO <sub>2</sub> / 235 g MgCl <sub>2</sub> / 275 g CaCl <sub>2</sub> + moisture added by humidity (approximate mixture after calcination)	4490	air	Effect of water salts
9	20 % Pu / 50% U/H <sub>2</sub> O <0.5%	1134 g PuO <sub>2</sub> / 3866 g U <sub>3</sub> O <sub>8</sub> <sup>d</sup>	1134	Helium	Baseline Mixed Oxide - Uranium effect (RFP Inert packaging)

a) all % by weight. b) Conainter will be filled with 5 kg oxide or to fill line dependent on density.

c) 84 - 88 wt% Pu d) MIS mixture - 2.8 kg, then fill remainder with uranium oxide.

### III. Evolved Issues.

During the course of the project, critical issues have developed and have been addressed. The issues discussed here have in combination, created significant delays in the project schedule. They are related to two sources: one is facility infrastructure requirements and the second is unforeseen project developments.

#### Facility Issues.

Accomplishments towards work in a nuclear facility are deliberate, tedious and carefully planned, approved and executed with great attention to safety and detail. Several unexpected events occurred that affected the facility and subsequently created scheduling delays. In resolving all the listed facility issues, the 94-1 Program did not have Facility Priority and therefore did not have the facility craft resources available to continue work or address many of the project specific issues in a timely manner.

The facility issues include the following: 1) A Pu-238 release and worker uptake in trouble-shooting compression fittings on some gas lines resulted in a Type A investigation and stand down of the facility. The incident, the DOE response, and the compensatory actions resulted in a significant loss of project time resulted. Prior to restarting work in the facility all employees were required to participate in Swagelock training, and all compression fittings in the facility had to be checked and bar coded (a multi-month process). 2) During this time, the facility was shut down again as a result of the Cerro Grande Fire. The recovery from the Cerro Grande Fire and the restart of the



facility was very lengthy. Procedures, materials and processes were checked and restarted with limited facility resources. Lack of priority again delayed project work until early in the calendar year. 3) The recommendations from the Type A investigation from the Pu release and the fire resulted in the implementation of highly evolved work control plans. The facility required that all Safe Operating Procedures (SOPs) be converted to Hazard Control Plans with specific Work Instructions. There was a lack of clarity and guidance from facility management on format and content for the required documents. 4) Additionally, during this time, the Laboratory experienced major security incidents, which resulted in a Laboratory shutdown to reevaluate the handling of classified information. Subsequently, the Laboratory changed the procedures for handling classified information, which became more formalized. Many safeguards were established for handling and preparing classified documents that affected key project team members and their productive work hours. Conservatively, these combined facility issues have contributed to approximately nine months delay in the project's schedule.

### **Project issues.**

Several unexpected technical issues developed during the course of the project that also contributed to schedule delays and included the following: 1) The welding of the modified can lid to the 3013 inner container was technically more difficult than anticipated. The difficulties encountered were a combination of a change in TIG welding personnel, and unfavorable welding test results. This resulted in a major change to the lid design. Our original design was approved by an ARIES welder, who was removed from the ARIES project for deviating from welding protocols to another position. Testing on the actual welding equipment and containers with the new certified and qualified welding personnel indicated that the original container lid design was inadequate to allow a quality weld to be completed. The old design did not allow the TIG weld tip to approach the material at a 90-degree angle. Thus, to compensate for welding at an oblique angle, the operation was done at extremely high temperatures, which created a deformation of the container lid. Micrographs of the original weld cross-sections were reviewed by MST-6, Mark Cola, for recommendations. The results indicated that a redesign of the lid was necessary and a new lid design was fabricated and tested that allowed for a simple butt-weld to be performed. The new set of weld micrographs indicated that a quality weld could be achieved with the new lid design. The weld parameters have been established and will be used for sealing the oxide containers.

2) Limited craft resources in the facility were problematic and our team implemented a new facility approach for completing glove box modifications. Our team received approval to prepare, test, and change out three glove box access panels for the project's glove boxes. The glove box access panels contain the feed-thrus that are required for the equipment operation and data acquisition. The glove box access panels were installed per approved established procedures. During this period of time, a new facility systems engineer was assigned to the facility, and he determined that the established procedures were inadequate and he would not approve and certify the access panels. The new systems engineer for the facility required new procedures with post-modification testing by trained, qualified, and certified personnel with required specifications. An example is that a certified torque wrench must be used for tightening the bolts to 20 inch pound with

variance of 5 inch pound. After many discussions with the new facility systems engineer, a glove box access panel had to be replaced with a panel that was fabricated by a facility approved machine shop. A dye penetrant test was performed on all welds, the access panel was helium lead tested and the access panel was installed to facility specifications for glove box enclosures with post- modification testing. All work was performed and documented by trained, qualified and certified personnel. The facility systems engineer under a non-conformance report accepted the two other access panels. The change in systems engineers and facility requirements created a two-month delay in testing the surveillance equipment.

3) An issue developed with the burst disk (a facility safety significant feature) and the related pressure analysis for the containers. The authorization basis documentation originally specified a 125 psig burst disk with a 1/2 inch opening [ESA-EPE-00-67]. A 125 psig burst disk was specified to the manufacturer, yet a 130 psig burst disk with a 3/8 inch opening was delivered, where 130 psig was within original manufacturer's tolerances. This non-conformance generated a re-analysis of the original safety analysis by ESA. During the re-analysis, new information allowed clarification of some of the original assumptions, which resulted in a more conservative scenario [ESA-EPE-01-132].

The worst-case scenario that was required by the facility was the generation of a combustible mixture pressurized inside a sealed container. Deflagration of this mixture generates a pressure pulse. In the original assumption, the deflagration was a  $H_2$  / air combustion, which would generate a maximum pressure ratio of 8. For this experiment,  $H_2$  /  $O_2$  combustion is the worst-case scenario, yet not expected to be observed, which would generate a maximum pressure ratio of 10.9 [Moody 2001]. The original assumption also vented  $H_2$ . The current analysis vents  $H_2O$ , which generates a lower sonic velocity, limits the amount of mass for venting, and subsequently increases the pressure pulse within the container. The container design now requires a 1-inch burst disk with a 7/8 inch free flow diameter to mitigate the effect of this scenario.

A new structural analysis for the location of a large vent hole was performed. The analysis indicates that the larger burst disk should be located in the center of the lid with a collar for structural integrity, Figure 9.

The allowable pressure for the container was also re-analyzed. Initially, a modal analysis was done that indicated the can mass was too small to ignore a 3 msec pressure pulse, which would be generated in the deflagration. Further review of ASME Code Sect III App. F indicated that the allowable stress for single use vessels is 1.6 x yield strength (40 ksi), which allows a maximum 1 time pressure pulse of 440 psig. This determination allowed some relief in the container structural analysis. Application of the ASME Code for continuous use, defines the maximum operating pressure of 184 psig.

The described re-analysis for the safety significant feature was presented to the Authorization Basis Group (NMT-14). Approval to continue and prepare for the Readiness Assessment was given.

4) The most recent project related issue was the development of leak checking capabilities for the sealed containers. An original agreement with ARIES personnel

included a leak check with their equipment after the lid is welded to the container bottom in the glove box. Recently, ARIES de-activated their glove box leak checking capabilities. This required our project to establish a method to check for container leaks after the final weld. A method using both pressure monitoring (rate of pressure loss) and He leak checking with a mass spectrometer allows the determination of a leak. We have specified an acceptable leak rate of 0.1 Torr per day (36 Torr per year) that the containers must meet.

## V. Future Work.

*Fiscal Year 2002.* In fiscal year 2002, the PF-4 Authorization Basis for this surveillance effort will be obtained by conduction and participation in a Readiness Assessment with DOE. Gas sampling and analysis on large and small oxide sample containers will begin on a routine basis. This effort consists of loading and monitoring up to 20 MIS oxide materials in small-scale containers that are representative of items in site-wide stabilization campaigns. The remaining 25 will be loaded in fiscal year 2003. Additionally, five full-scale containers will be placed on the surveillance rack and monitored. These containers will be sealed with up to 5 kg of oxide material that represents site wide problematic material. The remaining 4 large-scale containers will be loaded in fiscal year 2003. Specific tasks include: continued fabrication of 9 full-scale instrumented cans; installation of ALARA shielding; installation of leak check capabilities in the staging box; data collection and interpretation from Raman, GC and mass spectrometry, temperature and pressure measurements. The milestones and deliverables are listed below.

<b>Milestones and Deliverables:</b>	<b>Date Due:</b>
• Quarterly Reports (4) and Year End Report (1)	
• Load first oxide container for full scale study	10/18/01
• Complete installation of small-scale equipment in PF-4	2/15/02
• Obtain PF-4 Authorization Basis for large scale study (complete RA)	2/28/02
• Load up to 20 small-scale samples in miniaturized (4.5 ml) 3013 surveillance containers that contain representative DOE site-wide oxide including sample blanks and replications. Remaining 25 will be loaded in FY03.	9/20/02
• Complete loading of four additional large scale containers	9/20/02
• Collect, interpret and report data of large and small-scale surveillance containers – input information into a final year - end report	9/28/02

*Outyears.* Work planned for outyears include continued monitoring and data analysis of the sealed small- and large-scale containers. Additionally, ongoing experiments from previously loaded containers may be terminated. The contents and containers of the terminated samples will be analyzed, the welds and metal will be examined for corrosion or any other damage and the material in the container will be evaluated to show that it

does not change over time. This work will be integrated with the LANL IPS effort. Dependent on site-wide needs and results from the self-life studies, more containers will be prepared and loaded into the open locations. It is anticipated that this cycle of work will be ongoing until the 3013 containers under long-term storage, start to be removed for future disposition pathways.

## VI. Summary.

In summary, the results of the work performed here will provide critical information to DOE and the sites to assure that representative stabilized materials in approved containers are safe in long-term storage. We will provide guidance on what may or may not cause a container to pressurize, understand the changes in gas composition over time, and study the effect of corrosive gas generation in the cans. This information from this project will also be important to the formation of a site wide surveillance program for the extensive amount of material packaged according to the DOE Standard.

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